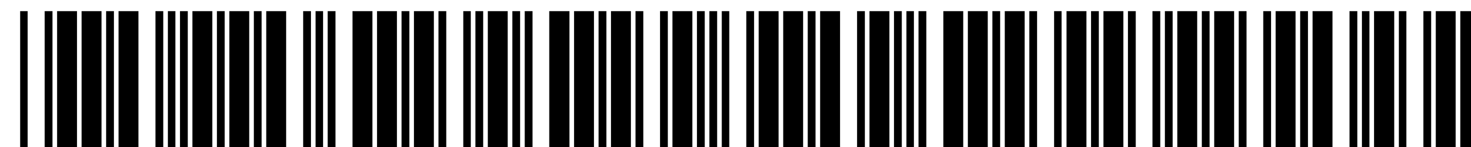


US010879081B2

(12) **United States Patent**
Jian et al.

(10) **Patent No.: US 10,879,081 B2**
(45) **Date of Patent: Dec. 29, 2020**

(54) **METHODS OF REDUCING OR ELIMINATING DEFECTS IN TUNGSTEN FILM**

(71) Applicant: **APPLIED MATERIALS, INC.**, Santa Clara, CA (US)

(72) Inventors: **Guoqiang Jian**, San Jose, CA (US); **Wei Tang**, Santa Clara, CA (US); **Chi-Chou Lin**, San Jose, CA (US); **Paul F. Ma**, Santa Clara, CA (US); **Kai Wu**, Palo Alto, CA (US); **Vikash Banthia**, Mountain View, CA (US); **Mei Chang**, Saratoga, CA (US); **Jia Ye**, San Jose, CA (US); **Wenyu Zhang**, San Jose, CA (US); **Jing Zhou**, Milpitas, CA (US)

(73) Assignee: **APPLIED MATERIALS, INC.**, Santa Clara, CA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **16/196,056**

(22) Filed: **Nov. 20, 2018**

(65) **Prior Publication Data**

US 2019/0157102 A1 May 23, 2019

Related U.S. Application Data

(60) Provisional application No. 62/590,053, filed on Nov. 22, 2017.

(51) **Int. Cl.**

H01L 21/321 (2006.01)
H01L 21/768 (2006.01)
H01L 21/285 (2006.01)

(52) **U.S. Cl.**

CPC ***H01L 21/321*** (2013.01); ***H01L 21/28556*** (2013.01); ***H01L 21/28568*** (2013.01); ***H01L 21/7685*** (2013.01); ***H01L 21/76877*** (2013.01)

(58) **Field of Classification Search**

None

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,482,740 B2 11/2002 Soininen et al.
6,727,169 B1 * 4/2004 Raaijmakers C23C 16/0272 438/622

(Continued)

FOREIGN PATENT DOCUMENTS

KR 10-2008-0060633 A 7/2008

OTHER PUBLICATIONS

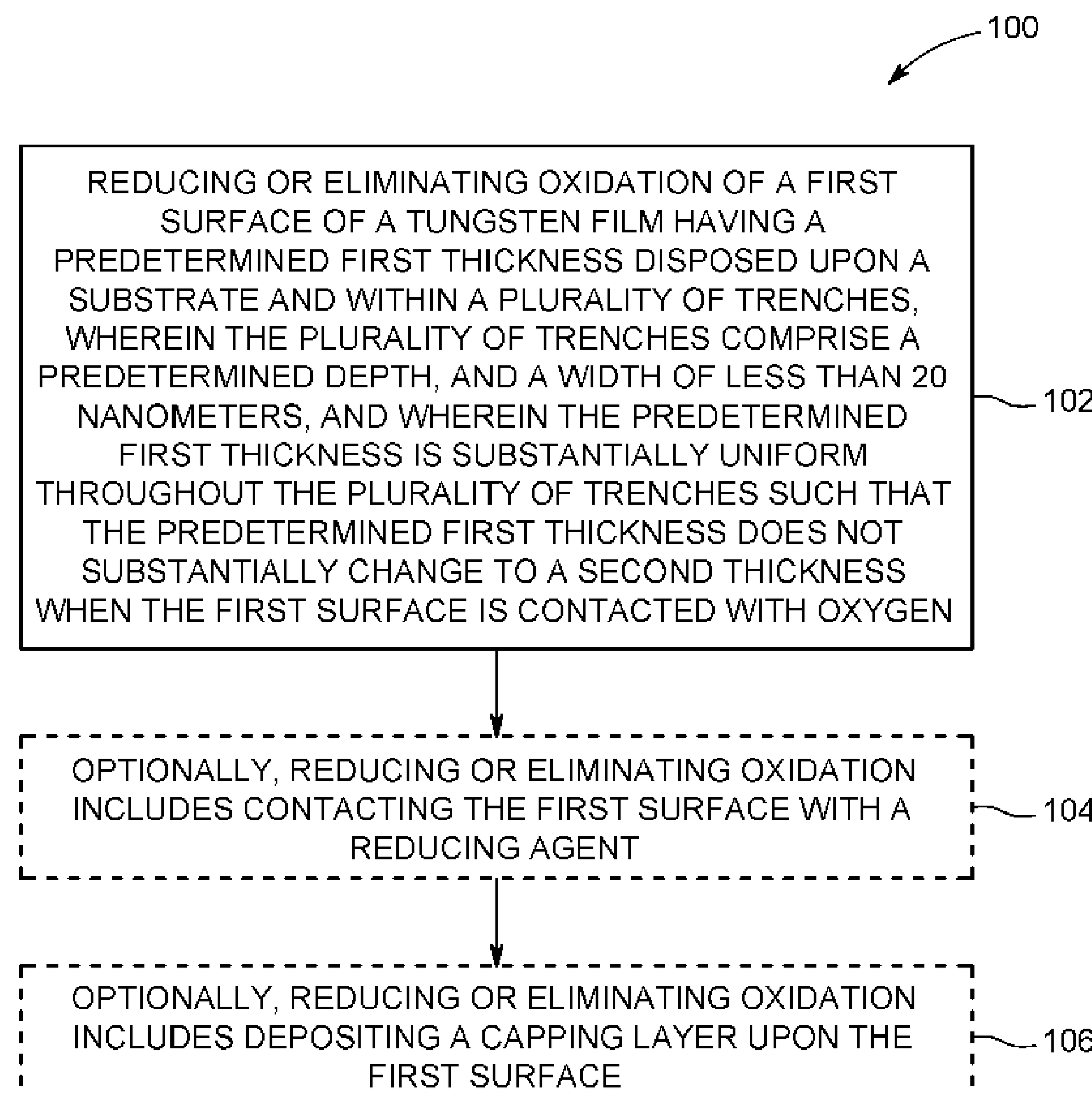
International Search Report and Written Opinion dated Mar. 8, 2019 for PCT Application No. PCT/US2018/061929.

Primary Examiner — Ali Naraghi
(74) *Attorney, Agent, or Firm* — Moser Taboada

(57) **ABSTRACT**

Methods and apparatus for reducing and eliminating defects in tungsten film are disclosed herein. In the present disclosure, reducing or eliminating oxidation of a first surface of a tungsten film having a predetermined first thickness disposed upon a substrate and within a plurality of trenches is disclosed. The plurality of trenches include a predetermined depth, and a width of less than 20 nanometers. The predetermined first thickness of the tungsten film is substantially uniform throughout the plurality of trenches such that the predetermined first thickness of the tungsten film does not substantially change to a second thickness when the first surface is contacted with air or oxygen.

20 Claims, 4 Drawing Sheets



(56) **References Cited**

U.S. PATENT DOCUMENTS

2006/0216932	A1*	9/2006	Kumar	H01L 21/7681 438/641
2014/0138602	A1	5/2014	Miller et al.	
2015/0050807	A1	2/2015	Wu et al.	
2015/0294975	A1*	10/2015	Nakata	H01L 27/10885 257/334
2016/0322493	A1	3/2016	Wang et al.	
2018/0138123	A1*	5/2018	Liang	H01L 23/5283

* cited by examiner

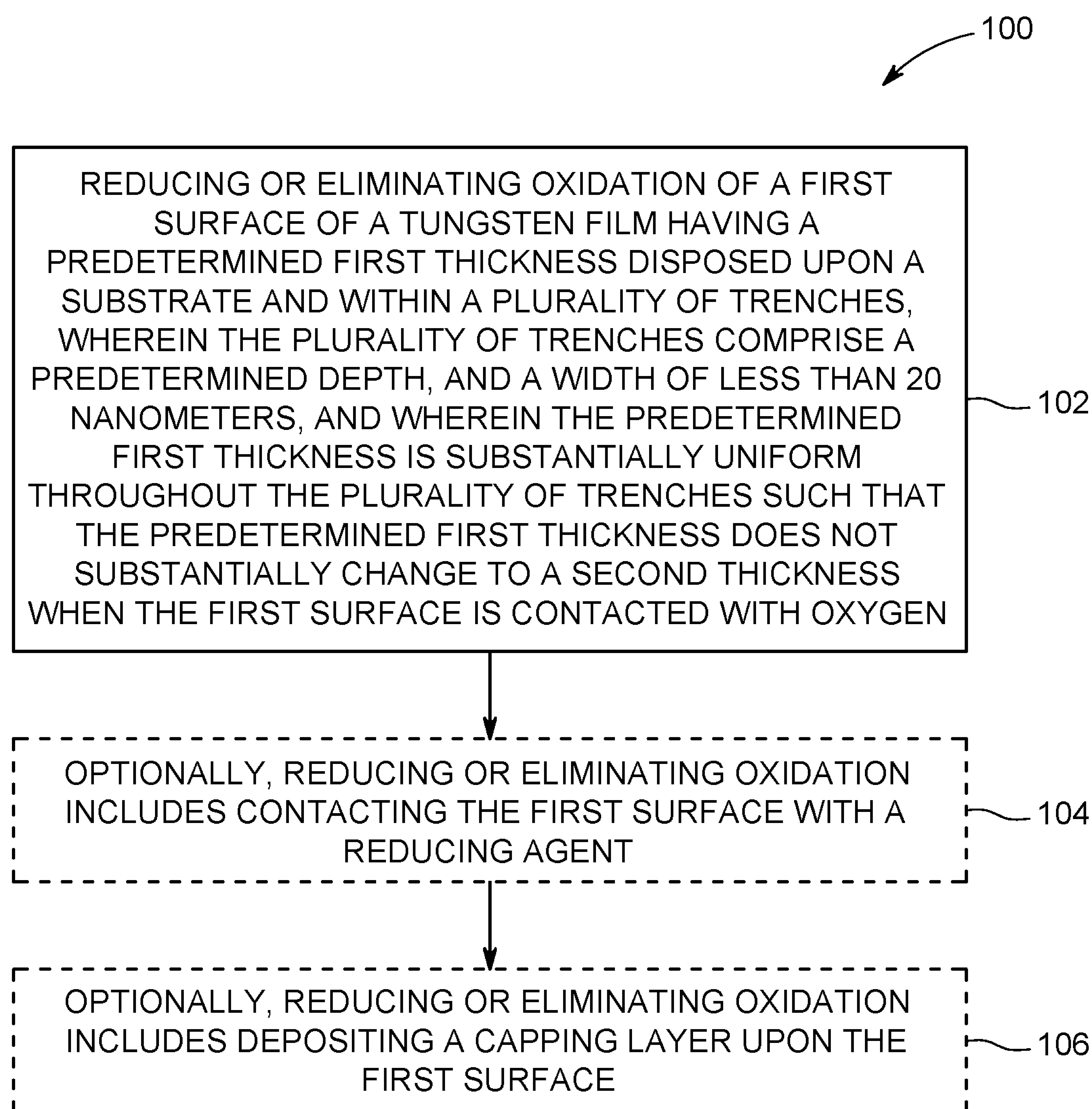


FIG. 1

FIG. 2A

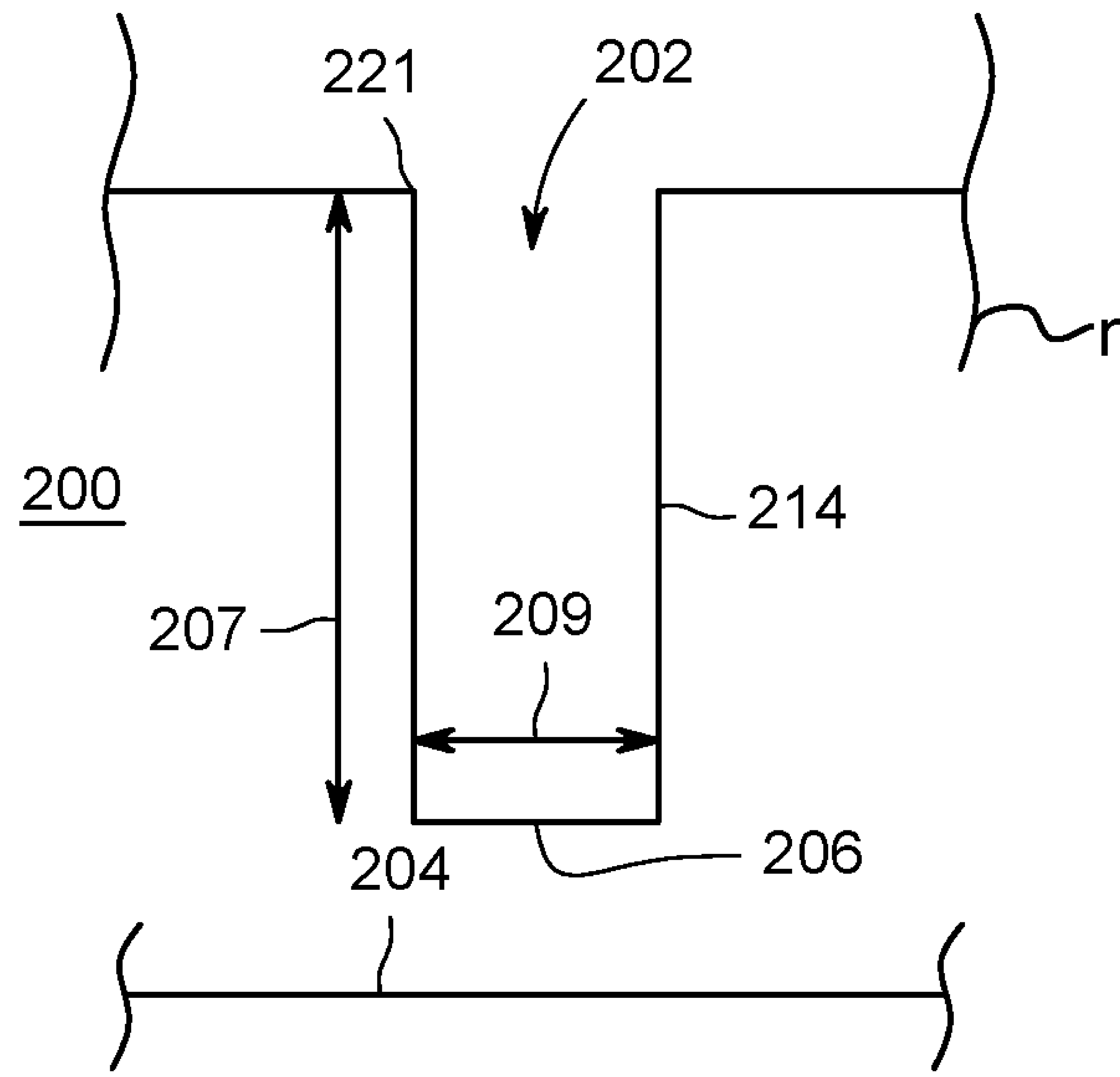


FIG. 2B

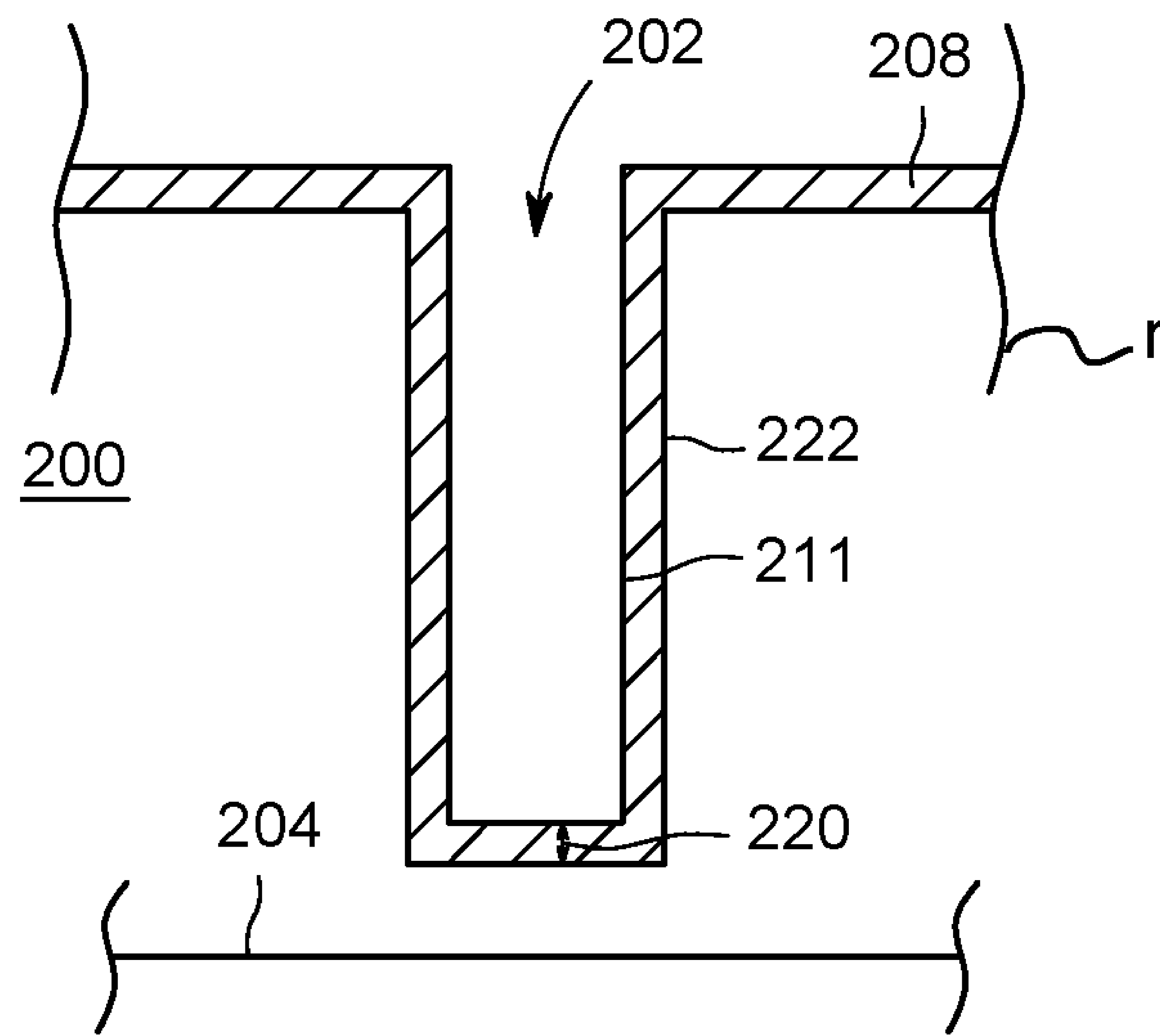
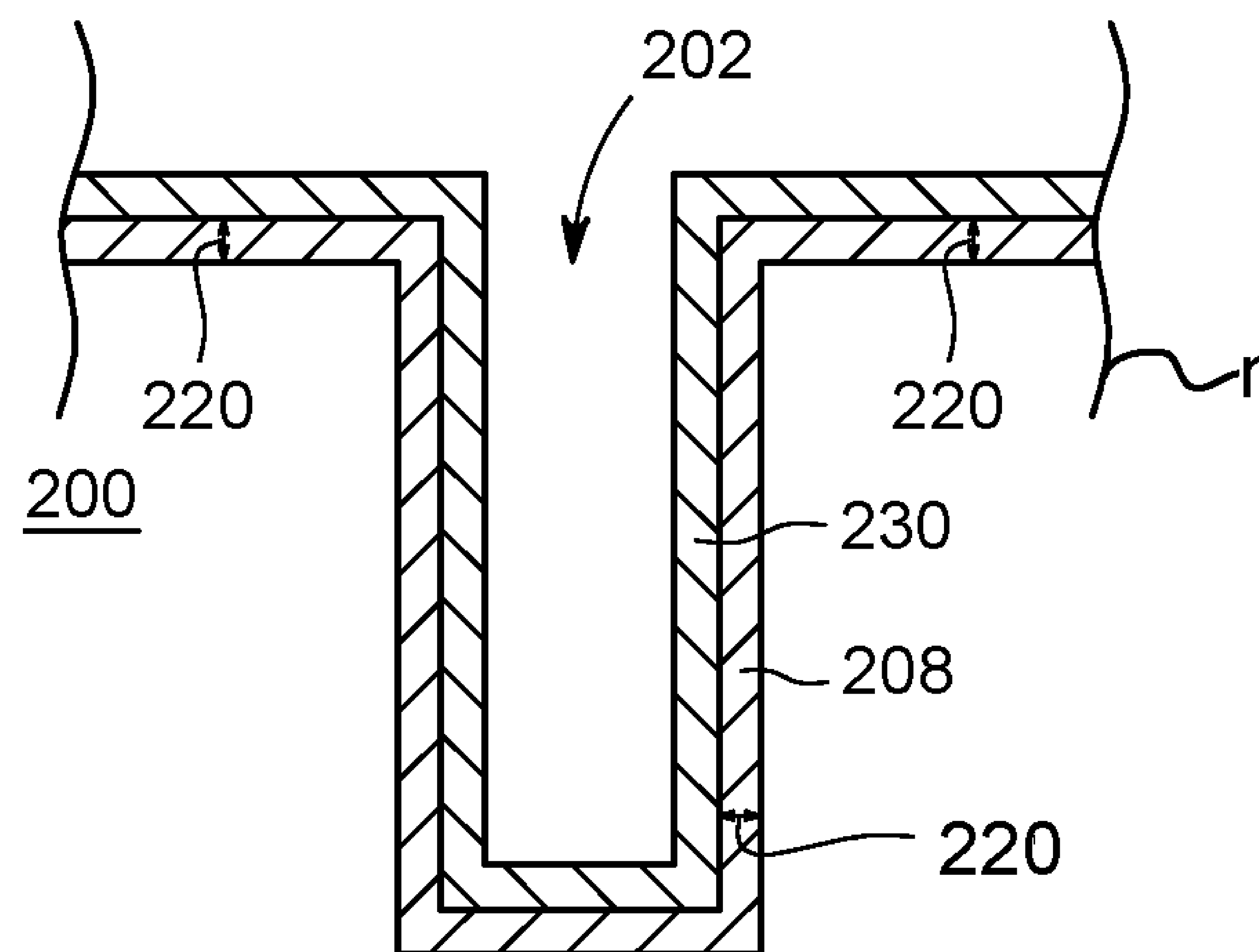


FIG. 2C



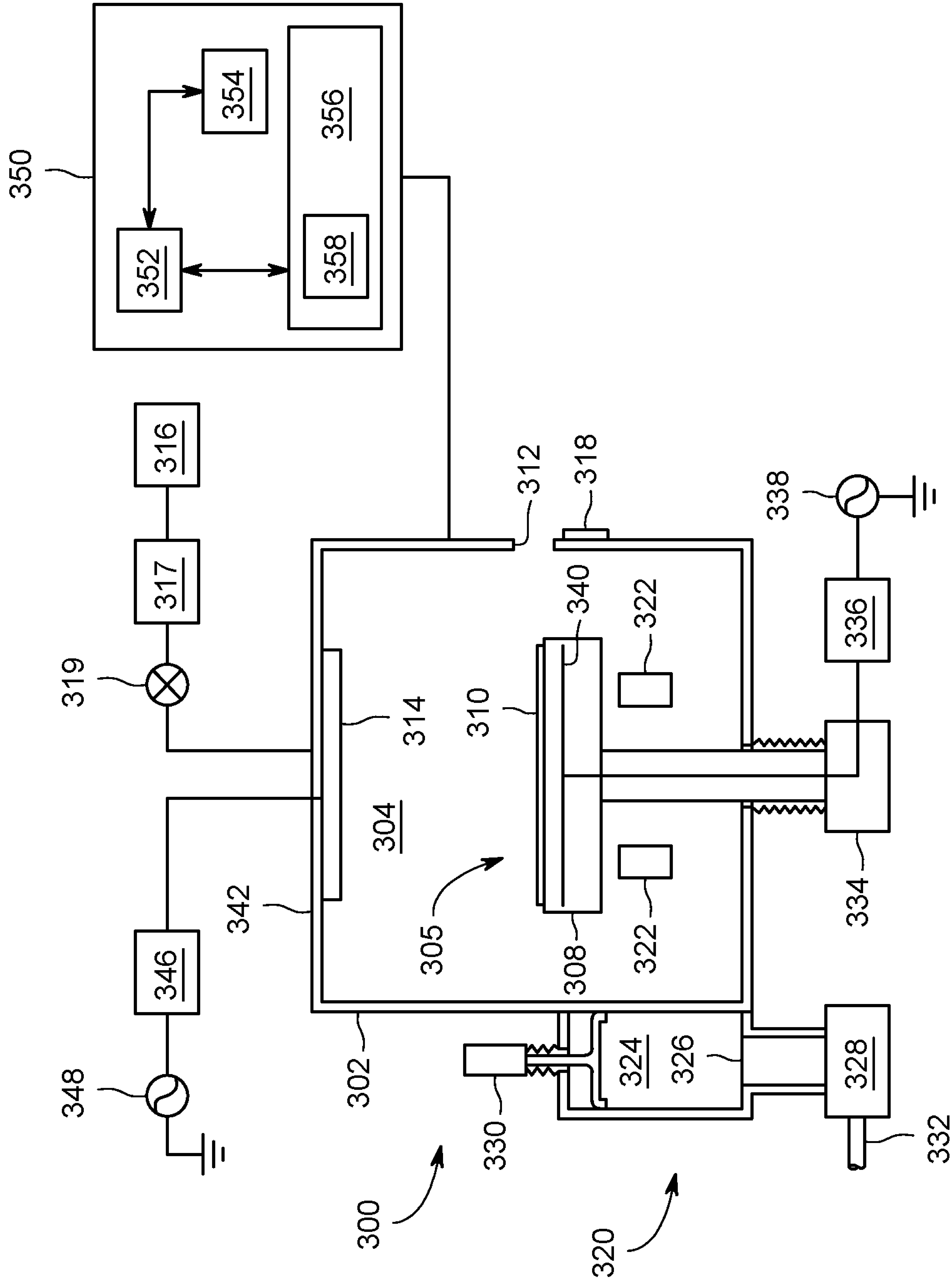


FIG. 3

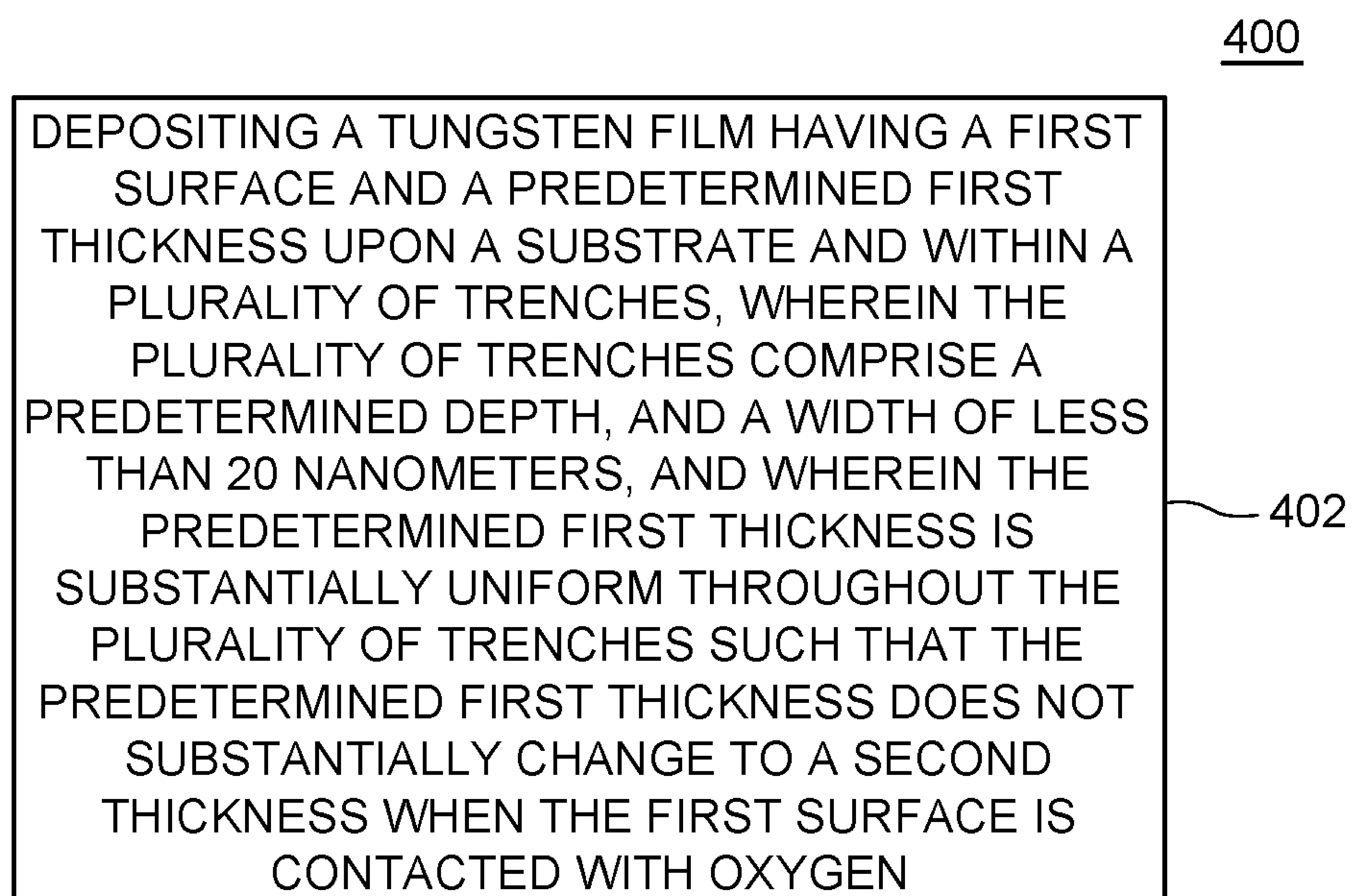


FIG. 4

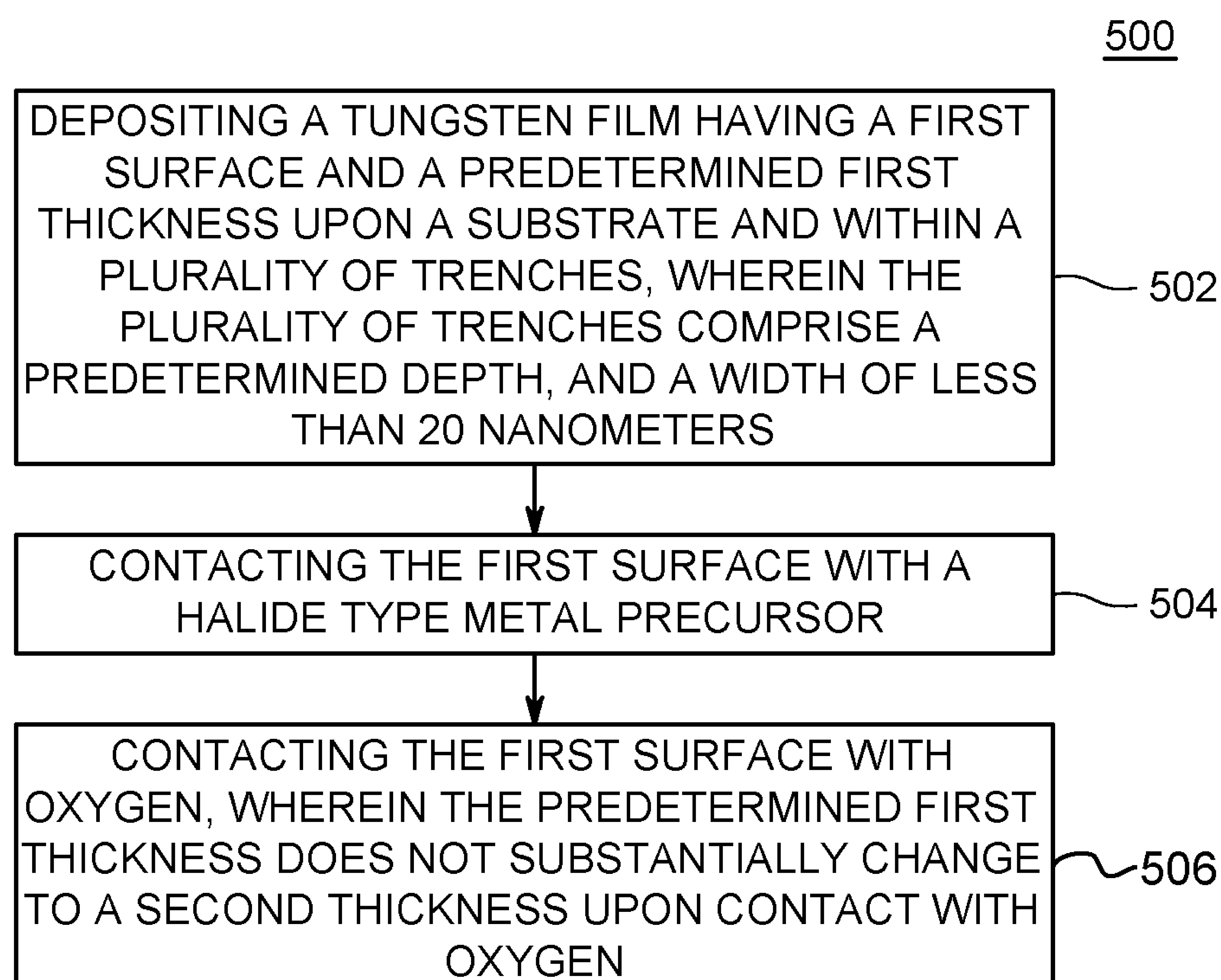


FIG. 5

METHODS OF REDUCING OR ELIMINATING DEFECTS IN TUNGSTEN FILM

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims benefit of U.S. provisional patent application Ser. No. 62/590,053, filed Nov. 22, 2017 which is herein incorporated by reference in its entirety.

FIELD

Embodiments of the disclosure generally relate to the processing of semiconductor substrates. More particularly, embodiments of the disclosure relate to deposition of tungsten layers on semiconductor substrates using vapor deposition techniques.

BACKGROUND

The semiconductor processing industry continues to strive for larger production yields while increasing the uniformity of layers deposited on substrates. These same factors in combination with new materials also provide higher integration of circuits per unit area of the substrate. As circuit integration increases, the need for greater uniformity and process control regarding layer thickness rises. As a result, various technologies have been developed to deposit layers on substrates in a cost-effective manner, while maintaining control over the characteristics of the layer.

Chemical vapor deposition (CVD) is one of the most common deposition processes employed for depositing layers on a substrate. CVD is a flux-dependent deposition technique that includes precise control of the substrate temperature and the precursors introduced into the processing chamber in order to produce a desired layer of uniform thickness. These process parameters become more critical as feature size, such as trenches and vias decrease, creating a need for more complexity in maintaining uniformity.

A variant of CVD that demonstrates excellent step coverage is cyclical deposition or atomic layer deposition (ALD). Cyclical deposition is based upon atomic layer epitaxy (ALE) and employs chemisorption techniques to deliver precursor molecules on a substrate surface in sequential cycles. The cycle exposes the substrate surface to a first precursor, a purge gas, a second precursor and the purge gas. The first and second precursors react to form a product compound as a film on the substrate surface. The cycle is repeated to form the layer to a desired thickness.

The inventors have found that depositing tungsten by conventional CVD and ALD methods, however, has several disadvantages. For example, defects are the primary device killers formed during semiconductor device manufacturing leading to device yield loss. As semiconductor devices features shrink to sub-20 nanometer regime, the inventors have observed new defects in logic metal gate and contact, NAND, and other memory structures. In tungsten related vapor deposition process (ALD and CVD), a type of defect is found in small trenches e.g. trenches having a width less than 20 nanometers. For example, silky-like defects may form in the lower portion of the feature or trench including WOx (in embodiments x is an integer such as 1-3) defects formed after tungsten or tungsten film, such as those formed from organic based process(es), are contacted with or exposed to air or oxygen. The defect appears as a silky-like deposit or residue that may deform the conformity of the layer or appear as a deposit reducing the depth of the feature or trench compared to other features without the defect. The defects, such as silky-like defects, may not be typically observed in larger trenches, e.g. trenches having a width greater than 20 nanometers. Such defects are problematic to continued processing such as deposition, patterning, and the like. For example, use of tungsten frustrates the manufacturing process as defects on the lower surface of a narrow trench impede the ability to uniformly deposit additional layers or films thereon as needed. Moreover, the inventors have found that the silky-like defects are unpredictable and difficult to monitor and control.

Accordingly, the inventors have provided improved methods of depositing tungsten and tungsten containing layers.

SUMMARY

Methods and apparatus for deposition of tungsten layers on semiconductor substrates using vapor deposition techniques are provided herein. In some embodiments, a method for reducing or eliminating defects in tungsten film, includes: reducing or eliminating oxidation of a first surface of a tungsten film having a predetermined first thickness disposed upon a substrate and within a plurality of trenches, wherein the plurality of trenches comprise a predetermined depth, and a width of less than 20 nanometers, and wherein the predetermined first thickness is substantially uniform throughout the plurality of trenches such that the predetermined first thickness does not substantially change to a second thickness when the first surface is contacted with oxygen.

In some embodiments, a method of depositing a tungsten film, includes: depositing a tungsten film having a first surface and a predetermined first thickness upon a substrate and within a plurality of trenches, wherein the plurality of trenches include a predetermined depth, and a width of less than 20 nanometers, and wherein the predetermined first thickness is substantially uniform throughout the plurality of trenches such that the predetermined first thickness does not substantially change to a second thickness when the first surface is contacted with oxygen.

A method of reducing or eliminating defects in tungsten film, includes: depositing a tungsten film having a first surface and a predetermined first thickness upon a substrate and within a plurality of trenches, wherein the plurality of trenches include a predetermined depth, and a width of less than 20 nanometers; contacting the first surface with a halide type metal precursor; and contacting the first surface with oxygen, wherein the predetermined first thickness is substantially uniform throughout the plurality of trenches such that the predetermined first thickness does not substantially change to a second thickness upon contact with oxygen.

Other and further embodiments of the present disclosure are described below.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the present disclosure, briefly summarized above and discussed in greater detail below, can be understood by reference to the illustrative embodiments of the disclosure depicted in the appended drawings. However, the appended drawings illustrate only typical embodiments of the disclosure and are therefore not to be considered limiting of scope, for the disclosure may admit to other equally effective embodiments.

FIG. **1** depicts a flow diagram of reducing or eliminating defects in tungsten film in accordance with embodiments of the present disclosure.

FIGS. **2**A-**2**C respectively depict stages of fabrication of depositing a tungsten film in accordance with embodiments of the present disclosure.

FIG. **3** is a process chamber suitable for performing a deposition process in accordance with some embodiments of the present disclosure.

FIG. **4** is a flow diagram of a method of depositing a tungsten film in accordance with one embodiment of the present disclosure.

FIG. **5** is a flow diagram of a method of reducing or eliminating defects in tungsten film in accordance with one embodiment of the present disclosure.

To facilitate understanding, identical reference numerals have been used, where possible, to designate identical elements that are common to the figures. The figures are not drawn to scale and may be simplified for clarity. Elements and features of one embodiment may be beneficially incorporated in other embodiments without further recitation.

DETAILED DESCRIPTION

Embodiments of the present disclosure provide methods of reducing or eliminating defects in tungsten film. While not intended to be limiting of the disclosure, embodiments of the present disclosure are useful when depositing tungsten in one or more trenches having a width of 20 nanometers or below.

The inventors have observed that by reducing or eliminating oxidation of tungsten after deposition by CVD and ALD, defects that form in one or more trenches having a width of 20 nanometers or less can advantageously be reduced or eliminated. Reducing or eliminating defects in the completed tungsten layer leads to device yield increase, reduced manufacturing costs, and an increase in uniformity across a plurality of features during the formation of a semiconductor device. Increased uniformity enhances application of additional process layers as manufacturing continues. The inventors have also found that methods in accordance with the present disclosure advantageously reduce or eliminate the formation of silky-like or WOx defects when ALD and CVD are employed under different process conditions. Thus, embodiments of the present disclosure may advantageously be used during different CVD and ALD processes. In some embodiments, methods of the present disclosure advantageously provide tungsten films having significantly improved surface uniformity and production level throughput. In embodiments, high quality control is maintained upon tungsten film contact with air and oxygen.

FIG. **1** is a flow diagram of a method **100** for reducing or eliminating defects in tungsten film in accordance with some embodiments of the present disclosure. The method **100** is described below with respect to the stages of depositing a tungsten film as depicted in FIGS. **2**A-**2**C and may be performed, for example, in a suitable cluster tool and process chambers. Exemplary processing systems that may be used to perform the methods disclosed herein may include, but are not limited to, any of the ENDURA®, CENTURA®, or PRODUCER® brand processing systems, commercially available from Applied Materials, Inc., of Santa Clara, Calif. Non-limiting examples of suitable cluster tools and process chambers are disclosed in commonly-owned U.S. Pat. No. 7,405,158 entitled Methods for depositing tungsten layers employing atomic layer deposition techniques, issued Jul. 29, 2008 to Lai et al. Other process chambers, including the process chamber of FIG. **3**, and ones available from other manufacturers, may also be suitably used in connection with the teachings provided herein.

The method **100** is typically performed on a substrate **200** provided to a processing volume of a process chamber (e.g. inner volume **305** of the process chamber **302** of FIG. **3**). In some embodiments, as shown in FIG. **2**A, the substrate **200** includes one or more features such as trench **202** (one shown in FIGS. **2**A-C) to be filled with a tungsten layer **208** of the substrate **200**, trench **202** extending towards a base **204** of the substrate **200**. Although the following description is made with respect to one feature, the substrate **200** may include any number of features (such as a plurality of trenches **202**, vias or the like) as described below. For example, referring to FIG. **2**A, n refers to an integer representing a number of trenches **202** in substrate **200**. In embodiments, n may be 1 or more than 1 representing a plurality of trenches **202** in the substrate **200**. For example, if n=5, FIG. **2**A would be representative of five trenches such as trench **202** in a single substrate **200**.

The substrate **200** may be any suitable substrate having the trench **202** formed in the substrate **200**. For example, the substrate **200** may include one or more of silicon (Si), silicon oxide (SiO_2), or the like. In embodiments, the substrate **200** may include trench **202** formed in a dielectric layer. For example, a low-k material (e.g., a material having a dielectric constant less than silicon oxide, or less than about 3.9), or the like. In addition, the substrate **200** may include additional layers of materials or may have one or more completed or partially completed structures or devices formed in or on the substrate **200** (not shown). In embodiments, the substrate **200** may be, for example, a doped or undoped silicon substrate, a III-V compound substrate, a silicon germanium (SiGe) substrate, an epi-substrate, a silicon-on-insulator (SOI) substrate, a display substrate such as a liquid crystal display (LCD), a plasma display, an electro luminescence (EL) lamp display, a light emitting diode (LED) substrate, a solar cell array, solar panel, or the like. In some embodiments, the substrate **200** may be a semiconductor wafer.

The substrate **200** is not limited to any particular size or shape. The substrate can be a round wafer having a 200 mm diameter, a 300 mm diameter or other diameters, such as 450 mm, among others. The substrate can also be any polygonal, square, rectangular, curved or otherwise non-circular workpiece, such as a polygonal glass substrate used in the fabrication of flat panel displays.

The trench **202**, or a plurality of trenches or features may be formed by etching the substrate **200** using any suitable etch process. In some embodiments, the trench **202** is defined by one or more sidewalls **214**, a bottom surface **206** and upper corners **221**. In some embodiments, the trench **202** may have a high aspect ratio, e.g., an aspect ratio between about of about 5:1 and about 20:1. As used herein, the aspect ratio is the ratio of a depth of the feature to a width of the feature. In embodiments, the trench **202** has a width **209** less than or equal to 20 nanometers, less than or equal to 10 nanometers, or a width **209** between 5 to 10 nanometers, between 5 to 15 nanometers, or between 1 and 20 nanometers. In embodiments, width **209** is approximately 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, or 19 nanometers.

Referring to FIG. **2**A-C, an underlayer (not shown) may optionally be deposited on substrate **200** and within trench **202** in a process chamber (e.g. process chamber **302** of FIG. **3**) configured to deposit a layer. The underlayer can be a layer conformably formed along at least a portion of the

sidewalls **214** and/or bottom surface **206** of a feature such as trench **202** such that a substantial portion of the feature prior to the deposition of the layer remains unfilled after deposition of the layer. In some embodiments, the underlayer may be formed along the entirety of the sidewalls **214** and bottom surface **206** of the trench **202**. The underlayer may be a wetting layer provided to enhance the adherence of a metal layer disposed upon the underlayer.

Referring to FIG. **2**B, a tungsten layer **208** is shown deposited atop the substrate **200** and within the trench **202**. In embodiments, tungsten layer **208** includes tungsten or a tungsten alloy. The tungsten layer **208** may also include, however, other metals, metal alloys, and dopants, such as nickel, tin, titanium, tantalum, molybdenum, platinum, iron, niobium, palladium, nickel cobalt alloys, doped cobalt, and combinations thereof. In embodiments, the tungsten and tungsten-containing material is substantially pure tungsten, or tungsten with no more than 5% impurities. In embodiments, the tungsten layer **208** is a tungsten film or tungsten-containing film resulting from a CVD and/or ALD processing and may include a pure tungsten (W), tungsten nitride (WN), tungsten carbide (WC), tungsten carbonitride (WCN), tungsten silicide (W_kSi_l), or tungsten oxide (W_nO_m) film, wherein k, l, m, and n are integers which inclusively range from 1 to 6. In embodiments, the tungsten films may include nitride metals containing tungsten, or tungsten metals containing N or C. In embodiments, the tungsten layer **208** includes a nitride containing tungsten product. Non-limiting examples of suitable nitride containing tungsten product for use herein includes a tungsten nitride film (WN film), tungsten carbonitride film (WCN film), or tungsten nitride of a high nitrogen concentration (WNy, $y>0.1$). In embodiments, suitable tungsten film for use in accordance with the present disclosure includes tungsten, tungsten nitride of a low nitrogen concentration (WNx, $0<x\leq0.1$), tungsten carbide of a low carbon concentration (WCx, $0<x\leq0.10$), tungsten carbide of a high carbon concentration (WCy, $y>0.1$), tungsten carbonitride of any carbon and nitrogen concentration (WCN).

In some embodiments, as shown in FIG. **2**B, the tungsten layer **208** is deposited atop a surface **222** of the substrate **200** and within the trench **202** formed in the surface **222**. In embodiments, the tungsten layer **208** is deposited within a plurality of trenches on the surface of the substrate. The tungsten layer **208** may be deposited using any suitable ALD and/or CVD deposition process(es). Non-limiting examples of CVD processes suitable for deposition of the tungsten layer **208** are disclosed in commonly-owned U.S. Pat. No. 7,405,158 entitled Methods for depositing tungsten layers employing atomic layer deposition techniques, issued Jul. 29, 2008 to Lai et al. In some embodiments, the tungsten layer **208** is deposited via a CVD process using suitable tungsten precursors for forming tungsten-containing materials including ALD process(es) described in commonly-owned U.S. Pat. No. 7,405,158 entitled Methods for depositing tungsten layers employing atomic layer deposition techniques, issued Jul. 29, 2008 to Lai et al. under the process conditions disclosed therein. Suitable process conditions for depositing tungsten layer **208** include process conditions, such as temperature suitable to heat the substrate at a temperature in the range from about 100° C. to about 600° C., or in the range from about 200° C. to about 500° C., or in the range from about 300° C. to about 450° C. In embodiments, the process chamber is maintained at a pressure in the range from about 1 Torr to about 150 Torr, or in the range from about 5 Torr to about 90 Torr.

In some embodiments, the thickness of the tungsten layer **208** is predetermined such as about 20 angstroms to about 150 angstroms, or about 50 angstroms to about 150 angstroms. In some embodiments, the thickness of the tungsten layer **208** is predetermined such as about 5 angstroms to about 1000 angstroms, or about 10 angstroms to about 500 angstroms, or about 10, 20, 30, 40, 50, 60, 70, 80, 90, or 100 angstroms. In embodiments, the shape of the first tungsten layer **208** is substantially uniform and conformal as generally shown in FIG. **2**B. However, the inventors have observed problematic variation may occur and oxidized material such as silky-defects may form in trench **202** proximate the bottom of trench **202** upon contact with air and oxygen. As explained above, silky-like defects may form in the lower portion, such as lower half, or lower third of the feature or trench including WOx (wherein x is an integer) defects formed after tungsten or tungsten film, such as those formed from organic based process(es), are contacted with or exposed to air or oxygen. The defects may appear as a silky-like deposit or residue that may deform the conformity of the layer or appear as a deposit reducing the depth of the feature or trench compared to other features without the defect. The defects, such as silky-like defects, may not be typically observed in larger trenches, e.g. trenches having a width greater than 20 nanometers. Such defects are problematic to continued processing such as deposition, patterning, and the like. As described herein, embodiments of the present disclosure reduce or eliminate the defects and ensure that tungsten layer **208** remains substantially uniform and conformal after contact with air and/or oxygen. For example, in embodiments tungsten layer **208** has a predetermined first thickness and is substantially uniform throughout a single trench and/or a plurality of trenches such that the predetermined first thickness does not substantially change to a second thickness when the first surface is contacted with oxygen.

Referring to FIG. **1**, **2**A-B, embodiments of the present disclosure include a method **100** of reducing or eliminating defects in tungsten film, including at **102**: reducing or eliminating oxidation of a first surface **211** of a tungsten layer **208** such as film having a predetermined first thickness **220** disposed upon a substrate **200** and within a plurality of trenches **202**. In embodiments, the plurality of trenches (n) is an integer such as 1 or more representing a plurality of trenches in substrate **200**. In embodiments, the plurality of trenches **202** may include a predetermined depth **207**, and a width **209** of less than 20 nanometers. In embodiments, the predetermined first thickness **220** of tungsten layer **208** is substantially uniform throughout the plurality of trenches **202** such that the predetermined first thickness **220** does not substantially change to a second thickness when the first surface **211** is contacted with oxygen. For example, in embodiments, the predetermined first thickness **220** of tungsten layer **208** may be measured and determined to be substantially uniform throughout the plurality of trenches **202** such that the predetermined first thickness **220** does not substantially change to a second thickness when the first surface **211** is contacted with oxygen. In one example, the predetermined first thickness **220** (shown as an arrow in tungsten layer **208**) is about 150 angstroms, and remains substantially uniform (about 150 angstroms) throughout a plurality of trenches **202** such that the predetermined first thickness **220** does not substantially change to a second thickness when the first surface **211** is contacted with oxygen.

Referring to FIG. **1**, method **100** may include at **104** reducing or eliminating oxidation by contacting the first

5 10 15 20 25 30 35 40 45 50 55 60 65

surface **211** with a reducing agent. In embodiments, at **104**, the first surface **211** is exposed to a soak process lasting in a range from about 1 second to about 90 seconds, such as 30 to 60 seconds, or around 60 seconds. In embodiments, the soak process occurs under the same or substantially similar process condition, such as temperature and pressure of the CVD or ALD process that deposited the tungsten layer. A pulse of a reductant or reducing compound accompanied with a suitable carrier gas is introduced into the process chamber. The reducing gas may be the same compound as the gas used for the soak process or alternatively, the reducing gas may be a different compound, depending on the product throughput requirements and the device applications. For example, in embodiments, where the first surface **211** is tungsten film including a nitride containing tungsten product, suitable reducing agent may include a halide type metal precursor to provide a metal halide at the first surface **211**. Non-limiting examples of suitable halide type metal precursor includes at least one of $TiCl_4$, $TaCl_4$, and combinations thereof. In other embodiments, where the first surface **211** is tungsten film including nitride such as a tungsten nitride film (WN film), tungsten carbonitride film (WCN film), or tungsten nitride of a high nitrogen concentration (WNy, $y>0.1$) suitable reducing agent may include a silane precursor, such as SiH_4. In embodiments, a silane precursor may be suitable wherein the tungsten film includes tungsten, tungsten nitride of a low nitrogen concentration (WNx, $0<x\leq0.1$), tungsten carbide of a low carbon concentration (WCx, $0<x\leq0.10$), tungsten carbide of a high carbon concentration (WCy, $y>0.1$), tungsten carbonitride of any carbon and nitrogen concentration (WCN).

A pulse of purge gas may be introduced into the processing chamber to purge or otherwise remove any residual reducing compound.

Referring now to FIG. **2**C and method **100** at **106**, optionally, first surface **211** may include a capping layer **230** disposed thereon to reduce or eliminate oxidation of tungsten layer **208**. In embodiments, the shape of the capping layer **230** is substantially uniform and conformal as generally shown in FIG. **2**C. In embodiments, the capping layer **230** has a conformal nature and does not completely fill the feature or trench. Accordingly, the capping layer **230** may be shaped to accommodate additional layers disposed atop the capping layer top surface. Suitable capping layers **230** may contain a metal or metal nitride material that includes titanium, titanium nitride, titanium silicon nitride, tantalum, tantalum nitride (TaN), tantalum silicon nitride, and combinations thereof. In embodiments, capping layer includes at least one of TiN, TaN, TiSiN, TiAlC, and combinations thereof. A capping layer **230** may be formed by process techniques such as chemical vapor deposition (CVD), atomic layer deposition (ALD), physical vapor deposition (PVD), derivatives thereof and combinations thereof. The capping layer **230** may be deposited to a thickness of at least about 30 angstroms, such as in a range from about 30 angstroms to about 200 angstroms. In one example, a capping layer **230** is deposited on the first surface **211** by an ALD process by using TiN. In another example, a capping layer **230** is deposited on the first surface **211** by an ALD process by using TaN. In another example, a capping layer **230** is deposited on the first surface **211** by an ALD process by using TiSiN. In another example, a capping layer **230** is deposited on the first surface **211** by an ALD process by using TiAlC.

In embodiments, the capping layer **230** may be plasma densified prior to performing a subsequent fabrication process.

FIG. **3** depicts a schematic diagram of an illustrative apparatus of the kind that may be used to practice embodiments of the disclosure as discussed herein. The apparatus **300** may comprise a controller **350** and a process chamber **302** having an exhaust system **320** for removing excess process gases, processing by-products, or the like, from the inner volume **305** of the process chamber **302**. Exemplary process chambers may include any of several process chambers configured for thermal decomposition reactions, atomic layer deposition (ALD), or chemical vapor deposition (CVD), available from Applied Materials, Inc. of Santa Clara, Calif. Other suitable process chambers from other manufacturers may similarly be used.

The process chamber **302** has an inner volume **305** that may include a processing volume **304**. The processing volume **304** may be defined, for example, between a substrate support **308** disposed within the process chamber **302** for supporting a substrate **310** thereupon during processing and one or more gas inlets, such as a showerhead **314** and/or nozzles provided at predetermined locations. In some embodiments, the substrate support **308** may include a mechanism that retains or supports the substrate **310** on the surface of the substrate support **308**, such as an electrostatic chuck, a vacuum chuck, a substrate retaining clamp, or the like (not shown). In some embodiments, the substrate support **308** may include mechanisms for controlling the substrate temperature such as heating and/or cooling devices (not shown), and/or for controlling the species flux and/or ion energy proximate the substrate surface. In embodiments, the process chamber **302** may be an oxygen-free process chamber. In embodiments, substrate support **308** may be include a filament **340**, heating mechanism **336** and power source **338** sufficient to heat the substrate and facilitate tungsten precursor deposition in accordance with the present disclosure.

In some embodiments, the substrate support **308** may include an RF bias electrode (not shown). The RF bias electrode may be coupled to one or more bias power sources (one bias power source not shown) through one or more respective matching networks (matching network shown). The one or more bias power sources may be capable of producing up to 1200 W or RF energy at a frequency of about 2 MHz to about 60 MHz, such as at about 2 MHz, or about 13.56 MHz, or about 60 Mhz. In some embodiments, two bias power sources may be provided for coupling RF power through respective matching networks to the RF bias electrode at respective frequencies of about 2 MHz and about 13.56 MHz. The at least one bias power source may provide either continuous or pulsed power. In some embodiments, the bias power source alternatively may be a DC or pulsed DC source.

The substrate **310** may enter the process chamber **302** via an opening **312** in a wall of the process chamber **302**. The opening **312** may be selectively sealed via a slit valve **318**, or other mechanism for selectively providing access to the interior of the chamber through the opening **312**. The substrate support **308** may be coupled to a lift mechanism **334** that may control the position of the substrate support **308** between a lower position (as shown) suitable for transferring substrates into and out of the chamber via the opening **312** and a selectable upper position suitable for processing. The process position may be selected to maximize process uniformity for a particular process. When in at least one of the elevated processing positions, the substrate support **308** may be disposed above the opening **312** to provide a symmetrical processing region.

The one or more gas inlets (e.g., the showerhead **314**) may be coupled to a gas supply **316** for providing one or more process gases through a mass flow controller **317** into the processing volume **304** of the process chamber **302**. In addition, one or more valves **319** may be provided to control the flow of the one or more process gases. The mass flow controller **317** and one or more valves **319** may be used individually, or in conjunction to provide the process gases at predetermined flow rates at a constant flow rate, or pulsed.

Although a showerhead **314** is shown in FIG. **3**, additional or alternative gas inlets may be provided such as nozzles or inlets disposed in the ceiling or on the sidewalls of the process chamber **302** or at other locations suitable for providing gases to the process chamber **302**, such as the base of the process chamber, the periphery of the substrate support, or the like.

The apparatus **300** may utilize capacitively coupled RF energy for plasma processing. For example, the process chamber **302** may have a ceiling **342** made from dielectric materials and a showerhead **314** that is at least partially conductive to provide an RF electrode (or a separate RF electrode may be provided). The showerhead **314** (or other RF electrode) may be coupled to one or more RF power sources (one RF power source **348** shown) through one or more respective matching networks (matching network **346** shown). The one or more plasma sources may be capable of producing up to about 3,000 W, or in some embodiments, up to about 5,000 W, of RF energy at a frequency of about 2 MHz and/or about 13.56 MHz or a high frequency, such as 27 MHz and/or 60 MHz. The exhaust system **320** generally includes a pumping plenum **324** and one or more conduits that couple the pumping plenum **324** to the inner volume **305** (and generally, the processing volume **304**) of the process chamber **302**.

A vacuum pump **328** may be coupled to the pumping plenum **324** via a pumping port **326** for pumping out the exhaust gases from the process chamber via one or more exhaust ports (two exhaust ports **322** shown). The vacuum pump **328** may be fluidly coupled to an exhaust outlet **332** for routing the exhaust to appropriate exhaust handling equipment. A valve **330** (such as a gate valve, or the like) may be disposed in the pumping plenum **324** to facilitate control of the flow rate of the exhaust gases in combination with the operation of the vacuum pump **328**.

To facilitate control of the process chamber **302** as described above, the controller **350** may be any form of general-purpose computer processor that can be used in an industrial setting for controlling various chambers and sub-processors. The memory, or computer-readable medium, **356** of the CPU **352** may be one or more of readily available memory such as random access memory (RAM), read only memory (ROM), floppy disk, hard disk, or any other form of digital storage, local or remote. The support circuits **354** are coupled to the CPU **352** for supporting the processor in a conventional manner. These circuits include cache, power supplies, clock circuits, input/output circuitry and subsystems, and the like.

The methods disclosed herein may generally be stored in the memory **356** as a software routine **358** that, when executed by the CPU **352**, causes the process chamber **302** to perform processes of the present disclosure. The software routine **358** may also be stored and/or executed by a second CPU (not shown) that is remotely located from the hardware being controlled by the CPU **352**. Some or all of the method of the present disclosure may also be performed in hardware. As such, the disclosure may be implemented in software and executed using a computer system, in hardware as, e.g., an application specific integrated circuit or other type of hardware implementation, or as a combination of software and hardware. The software routine **358** may be executed after the substrate **310** is positioned on the substrate support **308**. The software routine **358**, when executed by the CPU **352**, transforms the general purpose computer into a specific purpose computer (controller **150**) that controls the chamber operation such that the methods disclosed herein are performed.

Referring now to FIG. **4**, a flow diagram of a method **400** of depositing a tungsten film in accordance with one embodiment of the present disclosure is shown. At process sequence **402**, the method includes depositing a tungsten film having a first surface and a predetermined first thickness upon a substrate and within a plurality of trenches, wherein the plurality of trenches include a predetermined depth, and a width of less than 20 nanometers, and wherein the predetermined first thickness is substantially uniform throughout the plurality of trenches such that the predetermined first thickness does not substantially change to a second thickness when the first surface is contacted with oxygen. In embodiments, depositing a tungsten film further includes contacting the first surface with a reducing agent. In embodiments, the reducing agent is halide type metal precursor to provide a metal halide at the first surface (such as $TiCl_4$, $TaCl_4$, and combinations thereof) or a silane precursor such as a silane precursor comprising, consisting essentially of, or consisting of SiH_4. In embodiments, the reducing agent is $TiCl_4$, $TaCl_4$, or combinations thereof contacted with the substrate in an amount sufficient to reduce the substrate and/or prevent the formation of silky defects as described herein, or the formation of the tungsten layer with varied, non-uniform thickness. In some embodiments, the tungsten film includes nitride containing tungsten products. In some embodiments, depositing a tungsten film further includes depositing a capping layer upon the first surface.

Referring now to FIG. **5**, a flow diagram of a method **500** of reducing or eliminating defects in tungsten film is provided. In embodiments, method **500** includes at **502** depositing a tungsten film having a first surface and a predetermined first thickness upon a substrate and within a plurality of trenches, wherein the plurality of trenches includes a predetermined depth, and a width of less than 20 nanometers. At **504**, method **500** includes contacting the first surface with a halide type metal precursor. At **506**, method **500** includes contacting the first surface with oxygen, wherein the predetermined first thickness does not substantially change to a second thickness upon contact with oxygen. In embodiments, the halide type metal precursor is one of $TiCl_4$, $TaCl_4$, or combinations thereof. In embodiments, the halide type metal precursor is provided to an inner volume of a process chamber in an amount sufficient to react with the first surface to reduce the first surface and/or prevent the formation of silky defects as described herein on the first surface, or prevent the formation of the tungsten layer with varied, non-uniform thickness upon contact with oxygen.

In embodiments, the tungsten film comprises a nitride containing tungsten product, for example, the nitride containing tungsten product may comprise, consist essentially of, or consist of a tungsten nitride film (WN film), tungsten carbonitride film (WCN film), or tungsten nitride of a high nitrogen concentration (WN_y, $y>0.1$).

In some embodiments, the tungsten film comprises, consists essentially of, or consists of tungsten, tungsten nitride of a low nitrogen concentration (WN_x, $0<x\leq 0.1$), tungsten carbide of a low carbon concentration (WC_x, $0<x\leq 0.10$),

tungsten carbide of a high carbon concentration (WCy, $y>0.1$), tungsten carbonitride of any carbon and nitrogen concentration (WCN).

In other embodiments, of the present disclosure a method of depositing a tungsten film, includes: depositing a tungsten film having a first surface and a predetermined first thickness upon a substrate and within a plurality of features, wherein the plurality of features comprise a predetermined depth, and a width of less than 20 nanometers, and wherein the predetermined first thickness does not substantially change to a second thickness when the first surface is contacted with oxygen. In embodiments, the predetermined first thickness is substantially uniform throughout the plurality of features such that the predetermined first thickness does not substantially change to a second thickness when the first surface is contacted with oxygen.

In other embodiments of the present disclosure a method of depositing a tungsten film includes depositing a tungsten film having a first surface and a predetermined first thickness upon a substrate and within a plurality of features, wherein the plurality of features include a predetermined depth, and a width of less than 20 nanometers; and reducing or eliminating oxidation of a first surface of a tungsten film by contacting the first surface with a halide type metal precursor, silane, or capping layer as described herein. In embodiments, the method includes contacting the first surface with oxygen, wherein the predetermined first thickness does not substantially change to a second thickness upon contact with oxygen.

The disclosure may be practiced using other semiconductor substrate processing systems wherein the processing parameters may be adjusted to achieve acceptable characteristics by those skilled in the art by utilizing the teachings disclosed herein without departing from the spirit of the disclosure. While the foregoing is directed to embodiments of the present disclosure, other and further embodiments of the disclosure may be devised without departing from the basic scope thereof.

The invention claimed is:

1. A method of fabrication on a substrate, comprising:
reducing or eliminating oxidation of a fully-formed tungsten-containing metal film comprising contacting the provided metal film with a reducing agent, the metal film having a predetermined first thickness disposed upon a substrate and within a plurality of trenches, wherein the plurality of trenches comprise a predetermined depth, and a width of less than 20 nanometers, and wherein the predetermined first thickness is substantially uniform throughout the plurality of trenches such that the predetermined first thickness does not substantially change to a second thickness when the first surface is contacted with oxygen.

2. The method of claim **1**, wherein the plurality of trenches comprises trenches with, an aspect ratio, depth to width, between about of about 5:1 and about 20:1.

3. The method of claim **1**, wherein the reducing agent is halide type metal precursor to provide a metal halide at a surface of the metal layer.

4. The method of claim **3**, wherein the halide type metal precursor is at least one of $TiCl_4$, $TaCl_4$, and combinations thereof.

5. The method of claim **3**, wherein the tungsten-containing metal film comprises a nitride containing tungsten product.

6. The method of claim **5**, wherein the nitride containing tungsten product comprises tungsten nitride (WN film), tungsten carbonitride (WCN film), or tungsten nitride of a high nitrogen concentration (WNy, $y>0.1$).

7. The method of claim **1**, wherein the reducing agent is a silane precursor.

8. The method of claim **7**, wherein the silane precursor comprises SiH_4.

9. The method of claim **7**, wherein the tungsten-containing metal film comprises tungsten, tungsten nitride of a low nitrogen concentration (WNx, $0<x\leq 0.1$), tungsten carbide of a low carbon concentration (WCx, $0<x\leq 0.10$), tungsten carbide of a high carbon concentration (WCy, $y>0.1$), tungsten carbonitride of any carbon and nitrogen concentration (WCN).

10. The method of claim **1**, wherein reducing or eliminating oxidation further comprises depositing a capping layer upon the metal layer.

11. The method of claim **10**, wherein the capping layer is TiN, TaN, TiSiN, TiAlC, or combinations thereof.

12. The method of claim **1**, wherein the width of the plurality of trenches is between 5 to 10 nanometers.

13. A method of fabrication on a substrate, comprising:
depositing a fully-formed tungsten-containing metal film having a first surface and a predetermined first thickness upon a substrate and within a plurality of trenches, wherein the plurality of trenches comprise a predetermined depth, and a width of less than 20 nanometers, and wherein the predetermined first thickness is substantially uniform throughout the plurality of trenches; and
contacting the deposited metal film with a reducing agent such that the predetermined first thickness does not substantially change to a second thickness when the first surface is contacted with oxygen.

14. The method of claim **13**, wherein the plurality of trenches comprises trenches with an aspect ratio, depth to width, between about of about 5:1 and about 20:1.

15. The method of claim **13**, wherein the reducing agent is halide type metal precursor to provide a metal halide at the first surface or a silane precursor.

16. The method of claim **15**, wherein the halide type metal precursor is $TiCl_4$, $TaCl_4$, and combinations thereof.

17. The method of claim **13**, wherein the tungsten film comprises nitride containing tungsten products.

18. The method of claim **13**, wherein depositing a tungsten film further comprises depositing a capping layer upon the metal layer.

19. A method of fabrication on a substrate, comprising:
depositing a fully-formed tungsten-containing metal film having a first surface and a predetermined first thickness upon a substrate and within a plurality of trenches, wherein the plurality of trenches comprise a predetermined depth, and a width of less than 20 nanometers;
contacting the first surface with a halide type metal precursor; and
contacting the first surface with oxygen, wherein the predetermined first thickness does not substantially change to a second thickness upon contact with oxygen.

20. The method of claim **19**, wherein the halide type metal precursor is one of $TiCl_4$, $TaCl_4$, and combinations thereof and wherein the plurality of trenches comprises trenches with an aspect ratio, depth to width, between about of about 5:1 and about 20:1.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 10,879,081 B2
APPLICATION NO. : 16/196056
DATED : December 29, 2020
INVENTOR(S) : Jian et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In the Claims

Column 11, Line 54, in Claim 2, delete “with,” and substitute therefore “with”

Signed and Sealed this
Twenty-sixth Day of January, 2021

Drew Hirshfeld
Performing the Functions and Duties of the
Under Secretary of Commerce for Intellectual Property and
Director of the United States Patent and Trademark Office